African Journal of Science and Technology (AJST)
Science and Engineering Series Vol. 12, No. 1, pp. 51 - 58

AN ASSESSMENT OF THE PRESENCE OF HEAVY METALS IN THE SEDIMENTS OF THE LOWER MVOTI RIVER SYSTEM

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ABSTRACT:- *Excessive levels of heavy metals present in aquatic systems are often a result of anthropogenic activities. Sediment analysis for this type of contamination is often preferred over the dynamic water column. Due to accumulation of these elements over time, sediment analysis can provide a pollution-history for the site. Heavy metals at elevated levels are potentially toxic to aquatic life, and, because they bio-accumulate in food webs, are also potentially detrimental to human life. This study assesses the presence of heavy metals in the lower Mvoti River and Estuary. Levels of aluminium, arsenic, chromium, copper, iron, lead, magnesium, manganese, nickel, titanium, vanadium and zinc were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The results show that the riverine and estuarine sites closest to industrial effluent discharge sites and informal settlements displayed the highest levels of heavy metal contamination. The results of the estuarine analysis were compared to current levels of heavy metals present in two other South African estuaries : the St. Lucia Estuary, also located on the north of KwaZulu Natal and the Swartkops Estuary in the Eastern Cape, as well as two international estuaries. Even though the lower Mvoti River and Estuary does experience some heavy metal sediment contamination, the above-mentioned comparisons illustrate the level of contamination is relatively low in comparison to other ecologically significant South African estuaries, and selected international estuaries. With respect to heavy metals, these results bode well for the Mvoti, a system historically reported to be in serious ecological degradation from other pollution sources.*

INTRODUCTION

Coastal seas inevitably receive much of the effluent of the world. Rivers are responsible for transporting a range of both dissolved and particulate matter from land into the sea (Klavins *et al*., 2000). These contaminants most often derived directly from human activities, are sometimes harboured in estuaries and other coastal embayments before being flushed out to sea. Contaminants like potentially toxic metals are introduced into the environment either naturally or anthropogenically , or both (Harikumar & Jisha, 2010). Despite being natural components of the earth's crust, the severity of contaminants like heavy metals in the environment has drastically increased, primarily due to anthropogenic activities (Harikumar & Jisha, 2010; Chen & Kandasamy, 2008).

Due to its variable physical and chemical properties, the sediment component of aquatic systems is often the larger accumulator, and acts as potential sinks of contaminants, (Sundarajen & Natesan, 2010). The presence of high levels of heavy metals in the sediments of a system is a possible indication of human-induced pollution, derived from anthropogenic activities, as opposed to natural processes like weathering and erosion (Binning & Baird, 2001; Klavins *et al*., 2000). According to Nriagu & Pacyna (1988) in Chen & Kandasamy (2008), human induced inputs of metals like arsenic, nickel and zinc into the environment are often more than twice the input of the same metals from natural sources. The presence of these elements when investigating heavy metal contamination, can be detected by analysing water, sediments or biota. However, analysis of sediments are often more reliable and advantageous than the water column, as sediments assimilate these pollutants over time, while the water column on the other hand, is fairly dynamic and experiences significant changes over space and time (Landajo *et al.*, 2004; Binning & Baird, 2001).

The absence or very low levels of contaminants in the water column may be due to the accumulation of heavy metals by the sediment component of the system over time. As a result of this sediment accumulation, some indication of the history of pollution in a system may be understood (Chatterjee *et al.*, 2006; Landajo *et al*., 2004; Binning & Baird, 2001). In aquatic systems the most common sources of heavy metals are usually industrial effluent discharge (Topalián *et al.*, 1999). As noted by Martin & Whitfield (1983), in Binning & Baird (2001), in addition, around 90% of the particulate material carried by rivers settles in estuaries and coastal areas.

Another important factor to consider when investigating heavy metal contamination of aquatic sediments is the relationship between pollutant contamination and sediment texture. The finer components of sediment, like clays and silts are more likely to carry and accumulate heavy metal and organic contaminants in aquatic systems as opposed to the larger components of the sediments (Palanques *et al*., 2008; Binning & Baird, 2001). This is due to their relatively high adsorption ability (Chatterjee *et al*., 2006). This adsorption is dependant upon physico-chemical factors of the system like pH, dissolved oxygen, and oxidation-reduction potential (Ghrefat & Yusuf, 2006). However, contaminants are not necessarily fixed to sediments and are often re-mobilised *via* various chemical, physical and biological processes (Landajo *et al*., 2004). Sometimes, they are released into the water column and become available to living organisms (Landajo *et al*., 2004). There is also potential for the bio-accumulation of these contaminants in food webs (Chatterjee *et al*., 2006; Jordao *et al*., 2007) resulting in possible detrimental effects to biota and humans (Harikumar & Jisha, 2010).

This study focuses on the heavy metal characterization of the lower reaches of the Mvoti River, located approximately 70 km north of Durban on the KwaZulu- Natal coastal zone. The lower Mvoti River flows through a highly modified region of northern KwaZulu Natal. Much of the catchment is under agriculture, and sugarcane farming is extensive in the lower regions. Despite being one of South Africa's relatively smaller systems, the Mvoti River is an important resource for a number of towns, settlements and industrial developments along its approximately 197km long course (Wepener, 2007). Hence the river is subjected to a range of effects and influences associated with human activities.

In the upper and middle catchment of the river, agricultural, rural and informal users dominate, whilst in the lower catchment a distillery, sugar mill, pulp and paper mill as well as the sewerage works associated with the coastal town of KwaDukuza (formerly known as Stanger) are the principal users of the Mvoti. Two large tributaries, the Ntshaweni and Mbozambo rivers enter the Mvoti in the lower reaches (Malherbe *et al.*, 2010). Prior to its confluence with the Mvoti River, the Ntshaweni River receives effluent discharge and return flow from milling processes located in the area , and the Mbozambo River is the recipient of treated sewage and waste water from the town of Stanger. A short distance downstream, the river- dominated Mvoti Estuary receives this water before it eventually drains into the Indian Ocean. Since estuarine systems receive and frequently accumulate these catchment-derived pollutants, and considering the relatively poor water quality the lower Mvoti River system experiences (Sukdeo *et al.*, 2010), the Mvoti estuary is a potential contaminant sink for heavy metals with possible adverse biotic effects.

Although there has been significant research conducted regarding heavy metal contamination within estuarine sediments, and despite the vast anthropogenic influences within the study region, a significant assessment of such contamination within the Mvoti Estuary has not previously been attempted. Considering these factors, an evaluation of the abundance of heavy metals in this river system would be beneficial for future management of the system. Hence the purpose of this study is to provide an assessment of the heavy metals present in the sediments of the lower Mvoti River and Estuary, and to compare these results with levels of heavy metals present in the St. Lucia estuary - another ecologically significant system also on the northern coast of KwaZulu Natal, but one that is regarded to be in fairly pristine condition.

MATERIALS AND METHODS

Sampling Sites

A total of eight sample sites in the lower Mvoti River system were selected, of which five were located within the estuary itself. The remaining three sites were within the lower reaches of the river, but upstream of the estuarine reaches.

The extraction of samples was carried out using a Polyvinylchloride (PVC) Pipe Sediment Extractor. At each site, samples were collected at three different points: one midstream, and others midway between the midstream point and either bank. As this study aimed to assess the most

Figure 1. Location of the Mvoti Estuary in relation to the St. Lucia and Swartkops Estuaries along the South African coastline

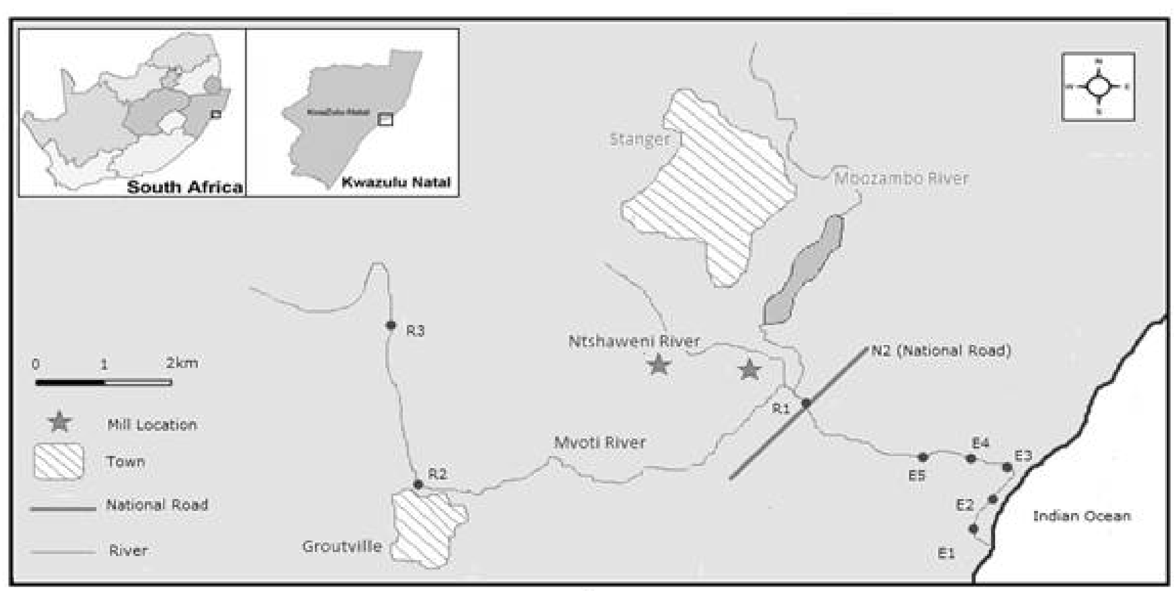

Figure 2. Map of the lower Mvoti River and estuarine system indicating the sampling sites selected for the study

recent heavy metal pollution due to increased anthropogenic activity, the upper 30 cm of the river and estuarine bed sediments were specifically sampled. Following collection, samples were sealed in polyethylene jars, stored at low temperatures, and sent for chemical analysis within 24 hours.

Sediment particle size analysis

Textural analyses to determine the particle size distribution of the samples was conducted in the soil science laboratory by using a standard dry sieving technique (Abed, 2006). Equal proportions of the three samples weighing approximately 500 g for each site were homogenised and oven-dried at 110ºC for 48 hours. Samples were then disaggregated using a pestle and mortar, and split using a riffle box sample splitter. One portion of the split samples were used to determine particle size using a Retsch sieve shaker, and the remaining portion was reserved for chemical analysis.

Chemical analysis to determine the heavy metal concentrations was carried out using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-OES) (Stoeppler, 1992 in Abed, 2006). According to Walsh (1997), in Abed (2006), ICP-OES measures atomic spectra of the elements being determined. Analysis by ICP offers a greater advantage in terms of sensitivity and freedom from interference. For the purpose of this study the following metals, namely, aluminium (Al), arsenic (As), chromium (Cr), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni), lead (Pb), titanium (Ti), vanadium (V) and zinc (Zn) were measured by the ICP- OES method.

Statistical analysis

The T-test was used to ascertain any differences between heavy metal concentrations in the sediments of the Mvoti and St. Lucia estuaries. Data for the St. Lucia Estuary from a prior study (Ajee, et al., 2010) was made available to this study for comparative purposes. All statistical analyses were completed using SPSS version 15.0 for Windows.

RESULTS AND DISCUSSION

The mean concentrations of heavy metals determined at each site are illustrated Table 1.

Table 1. Heavy metal concentrations (ppm) and mean (SE) at each sample site

Sample Site	Heavy metal concentrations (ppm) in the sediments of the estuarine section											
	Al	As	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Ti	V	Zn
Site E1	29.1	0.03	0.5	0	65.66	31.89	0.98	0	0.11	2.47	0.02	0
Site E2	50.6	0.37	0.11	0	64.99	40.23	1.27	0	0	5.8	0.1	0.07
Site E3	67.53	0	0.19	0.07	74.33	41.28	1.32	0.08	0.76	9.87	0.24	0
Site E4	58.69	0.17	0	0.22	123.96	42.05	0.98	0.11	0.97	16.14	0.39	0.1
Site E5	75.76	0.2	0.43	1.23	181.5	51.99	2.25	0.16	1.13	21.17	0.55	0.97
Mean (SE_x)	56.34	0.15	0.16	0.3	102.09	41.49	1.36	0.07	0.59	11.09	0.26	0.23
Sample Site	Mean (SE_x) heavy metal concentrations (ppm) in the sediments of the riverine section of the study area											
	Al	As	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Ti	V	Zn
Site R1	365.7	0.9	1.27	0.21	603.6	54.24	7.6	1.14	4.23	48.48	1.91	1.65
Site R2	57.01	0	0.92	0.03	211.14	22.44	1.34	0.06	0.13	26.79	0.44	0.54
Site R3	67.95	0	0.17	0	117.8	11.8	10.45	0	0.05	10.17	0.26	0.03
Mean (SE_x)	163.55	0.3	0.79	0.08	310.85	29.49	6.46	0.4	1.47	28.48	0.87	0.74

The upper reaches of the estuary, site E5 (Fig.1), displayed the highest levels of all the metals tested for within the estuarine section of the study area, with the exception of arsenic. This is the closest estuarine site where the Mvoti River experiences industrial discharge and utilization of the river for domestic purposes by informal settlements. At this point and at site E4, the estuary widens and decreases in depth due to excessive sedimentation, and becomes slow-flowing. The lagoon-like characteristics of E4 and E5 facilitate the settling of contaminants in this region. There is a general decrease in the concentrations of the heavy metals (with the exception of aluminium, which has a higher concentration at E3 than at E4) for the remaining estuary sites, approaching the Mvoti mouth. This decrease is signifcantly evident at site E1, closest to the Mvoti mouth, where levels of contaminants are at their lowest.

The highest concentrations of heavy metals tested for, with the exception of manganese, was experienced at sample site R1across both the riverine and estuarine sites. Site R1 was strategically chosen as it is directly under an N2 (national road) bridge and downstream at a point where the Mbozambo and Ntshaweni Rivers join the Mvoti. Effluent according to Malherbe (2006), from the pulp and paper mill, the sugar mill, and the Stanger sewage works enter into the Mvoti River slightly upstream of this site. In addition, the site is significantly influenced by informal communities, adjacent to the river, who use the river mainly for domestic purposes. In the vicinity of site R2 (located where the Mvoti River intersects the town of Groutville) the river is used extensively for domestic purposes as well as subsistence agriculture by the local community. This is possibly why the majority of heavy metal concentrations at this site were relatively higher in comparison to site R3. The lowest concentrations of heavy metals was recorded at site R3 (adjacent the Glendale Distillery). In contrast the highest concentration of manganese was recorded at this . The main use of the river at this point is the abstraction of water by the distillery, for use in its cooling processes thererafter in the irrigation of the surrounding sugarcane fields.

According to Ram *et al.* (2009), the grain size effect has significant bearing on the concentration of contaminants present within the sediment, therefore to compensate for this, the results were normalized for textural variations in sediment. The dependency of contaminant accumulation on sediment grain size is well documented (Palanques *et al*., 2008; Binning & Baird, 2001). This is clearly observed in both the estuarine and riverine sections of the study area where increases in contaminant concentrations are more likely associated with finer sediments. Estuarine site 5 has a higher concentration of heavy metals than the remaining estuarine sites which show decreases in concentration toward the river mouth. In addition, site 5 possesses higher amounts of fine sand and fines (very fine sand, silts and clays) compared to the other estuarine sites. Higher proportions of fine sediments located at sites away from the river mouth imply a proportional relationship between finer sediment and contaminant accumulation. The sediment composition of the Mvoti system is not typical of documented estuarine sediments, where the highest proportion of fines is found within the estuary. This is possibly due to the fact that the Mvoti is a perched, river-dominated system, with little or no significant marine influences. Hence there is a low accumulation of mud and fine sediments due to reduction in flocculation affected by low salinity. As a consequence of regular fluvial outflows, scouring of fine material is a common feature.

The site R1 with the highest percentage of fine sediment within the riverine section contains a high concentration of heavy metals. This unusually high proportion of finer sediment at the riverine sites (R1 in particular), most likely is a contribution from the Mbozambo and Ntshaweni rivers. Excessive siltation of the Mvoti River system according to Sukdeo *et al.*, (2010) is due to extensive and uncontrolled sandmining, riparian zone disturbances and agriculture along the river.

A similar study on the properties of sediments in the St. Lucia Estuary was conducted by Agjee *et al.* (2010). This system, located also on the north coast of KwaZulu Natal, is one of the most ecologically significant systems in South Africa due to its rich biodiversity. St.Lucia, a natural heritage site, is regarded as a fairly pristine environment but has recently been under threat of that status due to pressures from increased tourism and catchment activities. This is evident from the fact that five of the eight heavy metals analysed in a study by Agjee *et al.* (2010) correspond to those assessed in this study. Sample techniques and chemical methods of analysis are similar in both studies, thus enabling a comparison between the two estuaries. A comparison of heavy metals between the St Lucia by Agjee *et al.* (2010) and Mvoti estuaries are presented in Table 3.)

Table 3. Heavy metals (ppm) within the sediments of the St. Lucia Estuary (Agjee *et al*,. 2010) and the Mvoti Estuary

Estuary	Heavy metal concentrations (ppm)				
	Cr	Cu	Ni	Pb	Zn
St. Lucia	123.89	47	63.44	16	46.89
Mvoti	0.16	0.3	0.07	0.59	0.28
Mean	62.025	23.65	127.02	8.295	23.59
Std. Deviation	0.168	0.525	0.586	0.511	0.417
P- values	<0.05	<0.05	<0.05	<0.05	<0.05
*p-Value refers to the significant value obtained for the statistical procedure. Where $p < 0.005$, results are deemed significant					

The results of the statistical analysis show that significant differences exist between the two data sets illustrated in Table 3. The high concentrations of chromium and nickel according Agjee *et al.*, (2010), may be attribute to catchment geology. It has been suggested that these elements were mobilised and transferred into the system *via* leaching of minerals from the catchment area. Tributaries have also been known to be a potential source of these elements, and a protracted drought in the area has accelerated the accumulation of metals in the system (Agjee *et al.*, 2010). The concentrations of heavy metals are significantly higher within the sediments of the St. Lucia estuary, in comparison to the Mvoti Estuary.

The Mvoti Estuary has, by comparison, relatively lower levels of heavy metals (contaminants) than the other systems as shown in table 4. Shown also in table 4 is the mean concentrations of selected heavy metals present in two international estuaries, namely Galvesto Bay in Texas (Morse *et al.*,1993. In Binning & Baird, 2001), and Hudson-Raritan Estuary in New York Hence (Wolfe *et al.*, 1996. In Binning & Baird, 2001) , despite its reported polluted water quality status and the numerous other environmental problems which the estuary experiences (Sukdeo *et al.*, 2010), the sediments of the Mvoti estuary still demonstrates fairly low levels of heavy metal contamination in comparison to other important South African, as well as international systems.

Despite the data from these studies have been collected more than a decade ago it has been used as a comparator to show the superior status of current South African estuaries over its American rivals. This may be possibly attributed to relatively low metal contributions from catchment geology and less point anthropogenic sources of contamination. In addition, the Mvoti estuary itself as a perched estuary possess strong fluvial outflow that allows for continual flushing of sediments especially at the estuary mouth.

Table 4. Comparative amounts of heavy metals (ppm) within the sediments of two international and two South African estuaries

	Heavy metal concentrations (ppm)			
Heavy metal	Galvesto Bay (Texas)	Hudson-Raritan Estuary (New York)	Swartkops Estuary (South Africa)	Mvoti Estuary (South Africa)
Cr	37	122	20.3	0.16
Cu	8	142	6.8	0.3
Mn	605	No data available	115	1.36
Pb	25	160	33	0.59
Ti	No data available	21.7	99	11.9
Zn	55	299	36	0.23
*Galvesto Bay in Texas (Adapted from Morse *et al.*,1993. In Binning & Baird, 2001) *Hudson-Raritan Estuary in New York Hence (Adapted from Wolfe *et al.*, 1996. In Binning & Baird, 2001) *Swartkops Estuary in South Africa (After Binning & Baird, 2001)				

CONCLUSION

In this study it was found that that even though heavy metal contamination is present in the Mvoti system, it is relatively lower than those experienced by other selected estuaries. The distribution of heavy metals within the system is a possibility of primarily industrial effluent discharge into the system and domestic utilization of the river. However, further, in-depth analysis is required to confirm that these results are either due to domestic and industrial use in isolation, or the cumulative effect of improper catchment practices and management. The increased contamination and accumulation of heavy metals in riverine and estuarine sediments is a major cause for concern, as these elements are often remobilised into the water column and accumulate in food webs with detrimental end-results. It is therefore imperative to monitor the Mvoti sediments, thus preventing increasing levels of potentially toxic contaminants. This will also assist in improving the overall health condition of the system that is currently in an extremely poor condition.

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